

A first-principle study of half-Heusler alloys CKMg and SiKMg.

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Abstract

The structural, electronic, and magnetic properties of half-Heusler alloys CKMg and SiKMg are studied by using first-principle density functional theory. The calculations reveal the SiKMg alloy is a half-metallic ferromagnet with the magnetic moment of $1 \mu_B$ per formula unit at equilibrium lattice constant. The magnetic moment mainly originates from the strong spin-polarization of p electrons of Si atom and partial involvement of d electrons of K atom. The half-metallic gap is 0.105 eV. The robustness of half-metallic against the lattice constants for SiKMg is also calculated. CKMg alloy is nearly half-metallic with a spin polarization of 99.99 % at equilibrium lattice constant, but it is a good half-metallic alloy when a low pressure is applied. This shows CKMg is a very promising spintronic functional material.

Keywords: First-principle, half-Heusler alloy, Magnetic property, Pressure effect

1. Introduction

Half-metallic ferromagnets (HMF), of which one of the two channels shows metallic behaviour while the other shows the semiconductor or insulator behaviour at the Fermi level, have been attracting more and more interests due to their great potential applications in spintronic devices. Since the conception of the half-metal (HM) was introduced by de Groot et al. [1] in

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1983, many HMs have been found in a series of materials, such as ferromagnetic metallic oxides [2, 3, 4, 5], Heusler compounds [6, 7, 8, 9, 10, 11, 12], binary transition metal pnictides, chalcogenides with zinc-blended, rocksalt structures [13, 14, 15, 16, 17], etc.

Among these materials the half-metallic Heusler alloys are expected to play a key role in practical applications as a result of their very high Curie temperature and structural similarity compared to the widely used binary semiconductors crystallizing in the zinc-blended structure. Many researches have been made on these alloys. Based on first-principle electronic structure calculations, lots of them are predicted to be HMF. However, the half-metallic properties are difficult to obtain at room temperature because the half-metallic gap of the full-Heusler compounds is not very large. Furthermore, many half-metallic alloys which contain $3d$ transition metals usually have a big magnetic moment. They are not very suitable for spintronic device application, because the large magnetic moment means high stray fields and large energy losses. This defect motivates us to search for new HM materials which do not contain $3d$ transition metals.

Based on first-principle study, we investigate the stability in structure, magnetic and pressure effect of CKMg and SiKMg alloys. This kind of half-Heusler compounds which has the general formula XYZ and crystallizes in non-centrosymmetric cubic $\text{MgAgAs}(\text{C1}_b)$ structure with $\text{F}\bar{4}3m$ (space group No.216), has three interpenetrating *fcc* lattices. The corresponding Wyckoff positions are $r_1 = (0.00, 0.00, 0.00)$, $r_2 = (0.25, 0.25, 0.25)$, $r_3 = (0.75, 0.75, 0.75)$ [18], and each of the X, Y and Z atoms can occupy one of the three positions. Then interchanging the positions of atoms in the cubic structure, we can get three phases, which are $\alpha = (r_1, r_2, r_3)$ phase, $\beta = (r_3, r_1, r_2)$ phase and $\gamma = (r_2, r_3, r_1)$ phase, respectively.

2. Computational method

In this paper, we perform our calculations by using full-potential local-orbital minimum-basis code (FPLO) [19, 20]. The scalar relativistic exchange-correlation energy is treated within the generalized gradient approximation (GGA) [21]. The k mesh is performed as 24. Accurate Brillouin zone integrations are performed by using the standard special K point technique of the tetrahedron. The convergence criteria of a self-consistent field iteration is set to both the density (10^{-6} in code specific units) and the total energy (10^{-8} hartree).

3. Results and discussions

3.1. Structural properties

First, to get the equilibrium lattice constants of the half-Heusler alloys CKMg and SiKMg, we calculate the total energy as a function of lattice constants for the three possible atomic arrangements. Fig.1 shows the total energy curves with respect to the lattice constants of α , β , γ structures in the ferromagnetic (FM) and the nonferromagnetic (NM) phases for CKMg. Fig.2 is for SiKMg. From the two figures, we can get that for both alloys, the β structure is the most stable among the three in both FM and NM phases. Then we compare the total energies of the two alloys in the FM and NM phases of the β structure. The total energy-lattice constant relation curves are shown in Fig.3. It implies that the FM state is more stable than the NM state. We get the lattice constant of equilibrium is 6.345 Å for CKMg and 7.160 Å for SiKMg by using Murnaghan equation [22]. The equilibrium lattice constants, bulk modulus, the first order derivative of the modulus on volume, cohesive energy and formation energy we calculated are displayed in Table 1.

Formation energy (ΔH_{for}^{XKMg}) shows the stability of the compound with respect to decomposition into bulk constituents. For each alloy, the formation energy can be expressed by

$$\Delta H_{for}^{XKMg} = E_{total}^{XKMg} - (E_{bulk}^X + E_{bulk}^K + E_{bulk}^{Mg}), \quad (1)$$

Where E_{bulk}^X , E_{bulk}^K , and E_{bulk}^{Mg} are the total energies per atom for bulk X (X=C, Si), K and Mg, respectively. In general, a negative value of formation energy indicates compounds could be synthesized easily. Both the alloys are likely to be synthesized experimentally due to the negative formation energy (see Table.1).

The cohesive energies of the two alloys can be obtained from the equation:

$$E_{coh} = (E_{atom}^X + E_{atom}^K + E_{atom}^{Mg}) - E_{total}^{XKMg}, \quad (2)$$

where E_{total}^{XKMg} is the total energies of the considered compound, E_{atom}^X (X=C, Si), E_{atom}^K and E_{atom}^{Mg} are the energies of isolated constituent atoms in each compound. In general, a positive value of cohesive energy indicates the stability of the material. Therefore we can confirm the alloys we study are expected to be stable.

3.2. Electronic and magnetic properties

Fig.4 displays the total density of states of CKMg and SiKMg alloys under equilibrium lattice constants. From the figure we can see, for the SiKMg alloy, the spin-up states show semiconductor character while the spin-down states show metallic nature. So we can get that the SiKMg alloy is a half-metallic ferromagnet. The spin magnetic moments are $1 \mu_B$ for the two alloys per formula unit (See Table 1). There are 7 valence electrons in SiKMg alloy, and the total magnetic moment of $1 \mu_B$ per formula unit complies with the Slater-Pauling behavior of HM half Heusler alloys

$$M_{tot} = (8 - Z_{tot})\mu_B \quad (3)$$

where Z_{tot} is the number of total valence electrons and M_{tot} the total magnetic moment per formula unit. We offer the band gap and spin-flip gap in Table 1. Fig.5 displays the band structure of the SiKMg alloy. The band gap is formed by the valence band maximum (VBM) and the conduction band minimum (CBM) at Γ point.

Now, we have a discussion on the CKMg alloy. From Fig.4, we can see the density of states (DOS) in both the spin down and spin up band structures get through the Fermi level, so the half Heusler alloy is not a half-metal, but a nearly half-metal. According to the definition, the spin polarization(P) can be expressed by

$$P = \frac{N \downarrow (\varepsilon_F) - N \uparrow (\varepsilon_F)}{N \downarrow (\varepsilon_F) + N \uparrow (\varepsilon_F)}, \quad (4)$$

where $N \downarrow (\varepsilon_F)$ and $N \uparrow (\varepsilon_F)$ are the DOS of majority-spin and minority-spin at Fermi level, respectively. The values of $N \downarrow (\varepsilon_F)$ and $N \uparrow (\varepsilon_F)$ can be obtained from Fig.4. Through Eq.(4), we can calculate out that the spin polarization of the SiKMg alloy is 99.99 % under its equilibrium lattice constant. The spin polarization is so high that we can get the half-metallicity of the CKMg by applying a very low pressure, which will be discussed in section 3.4.

3.3. Stability of half-metallicity

HM materials are usually used in spintronic devices in the form of thin films or multilayers, the lattice constant will have a change when the films or multilayers are grown on appropriate substrate, and the corresponding half-metallicity may be destroyed. So it is meaningful to study the robustness

of the half-metallicity with respect to variation of the interatomic distance. Fig.6 gives the relation between the lattice constant and external pressure for the SiKMg alloy. Fig.7 shows the change of total magnetic moment as a function of the lattice constants and pressures. As mentioned previously, integer magnetic moments are a unique property of half-metallic. The total magnetic moment remains to be an integer with the lattice constant changes in the ranges of 5.90 Å to 7.16 Å. Namely SiKMg alloy can preserve half-metallic character when its lattice constant is changed by 17.6 %. From Fig.6 we can get that the critical lattice constant with half-metallic character is equivalent to add the external pressure of 25.22 GPa. Therefore, the SiKMg alloy has stable half-metallic character, and it could be applied in the thin films and layers for spin valves and magnetic tunnel junctions and can be used as electrodes in tunnel junctions.

3.4. *Effect of pressure*

From Fig.7, we can see for the SiKMg alloy, the magnetic moment keeps $1.00 \mu_B$ when the pressure is in the range from 0.00 GPa to about 25.22 GPa. When the external pressure is up to 35.99 GPa, the magnetic moment becomes zero, which indicates the transition from FM to NM state.

Fig.8 displays the density of states with different pressures of the SiKMg alloy. From the figure we can get that the p states of Si atoms make the main contribution to the density of states from -2.7 to 0 eV below the Fermi level, indicating the magnetic moment mainly carried by Si atoms, and the total states from 4 to 14 eV are mainly contributed by the d states of K atoms. A p - d hybridization occurs around the Fermi level. The Fermi level slowly shifts to the edge of VBM and finally passes through it, which means the changing from half-metallic to metallic characters.

As mentioned in section 3.2, the CKMg alloy has such a very high spin polarization that just by applying a very low pressure it may transform into a half-metal. In the following we will discuss the effect of pressure on the CKMg alloy. Fig.9 and Fig.10 show the changes of magnetic moment and band gap under pressure. From Fig.9, we can see, the magnetic moment keeps $1 \mu_B$ when pressure in the range from 0 GPa to 20.35 GPa. The magnetic moment becomes zero when the external pressure beyond 23.60 GPa. From Fig.10 we can get that CKMg will have a band gap just by applying a pressure of 0.23 GPa. This shows CKMg is a good spintronic functional material. In the range from 0.23 GPa to 20.35 GPa, CKMg keeps having band gaps, while upon 20.35 GPa, the gaps vanish. On the whole, CKMg alloy keeps being

HM when pressure in the range from 0.23 GPa to 20.35 GPa, a ferromagnet from 20.35 GPa to 23.60 GPa and a paramagnet beyond 23.60 GPa.

4. Conclusions

In this paper, we study the structural, electronic, and magnetic properties of half-Heusler alloys CKMg and SiKMg. Our results show the SiKMg alloy is a half-metallic ferromagnet. The half-metallicity can be preserved up to 17.6 % compression of lattice constant with respect to its equilibrium lattice constant. CKMg is a nearly half-metal with a very high spin-polarization of 99.99 % under its equilibrium lattice constant and it will transform into a half-metal when a low pressure of 0.23 GPa applied, showing CKMg is a very promising functional material. So our results will offer some valuable hints to spintronic material design and development.

Reference

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Table 1: Calculated equilibrium lattice (a_0), bulk modulus B , the first order derivative of the modulus on volume (B'), cohesive energy (E_{coh}), formation energy per unit cell (ΔH), total spin magnetic moment (M_t), band gap (E_{bg}), and spin-flip gap (E_{sfg}) are shown for SiKMg and CKMg, respectively.

XKMg	$a_0(\text{\AA})$	$B(\text{GPa})$	B'	$E_{coh}(\text{eV})$	$\Delta H(\text{eV})$	$M_t(\mu_B)$	$E_{bg}(\text{eV})$	$E_{sfg}(\text{eV})$
CKMg	6.345	13.3	4.12	6.02	-5.85	1.00	0.000	0.000
SiKMg	7.160	13.6	2.96	5.60	-5.41	1.00	0.949	0.105

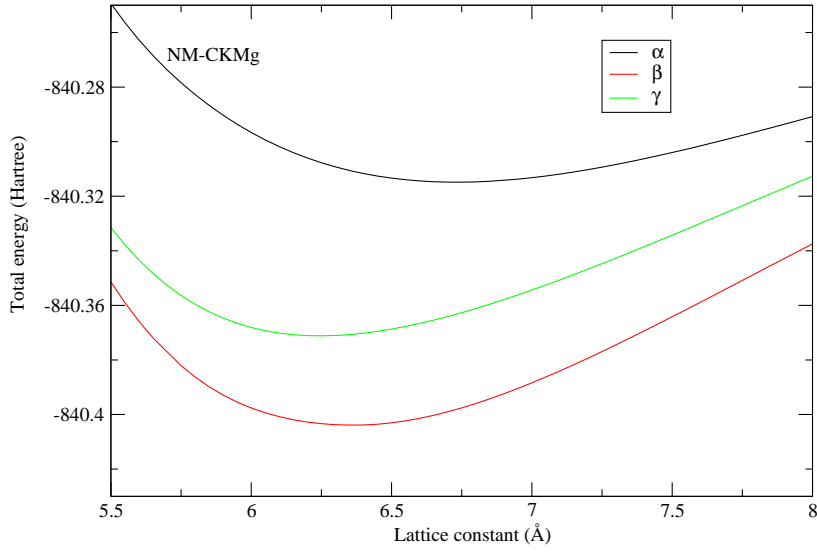
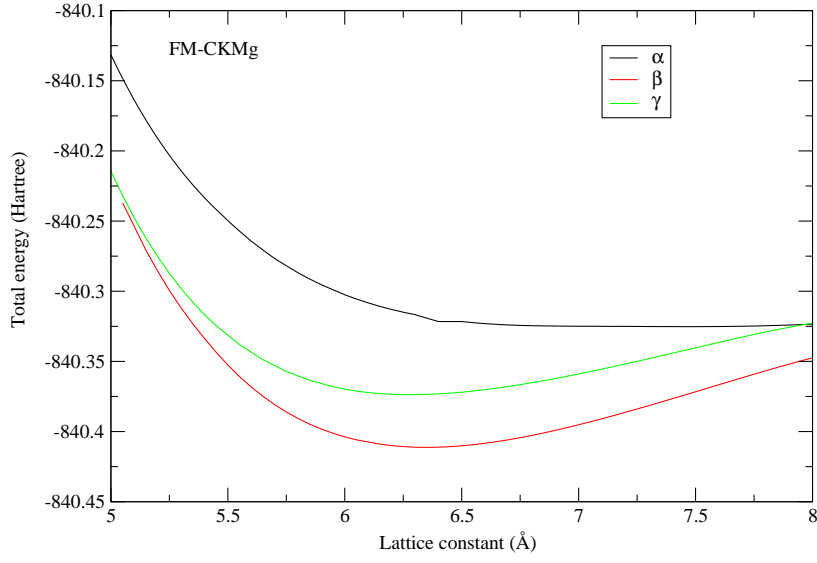


Figure 1: The total energies per unit cell as a function of lattice constants for α , β and γ structure for the CKMg in the FM phase and NM phase, respectively.

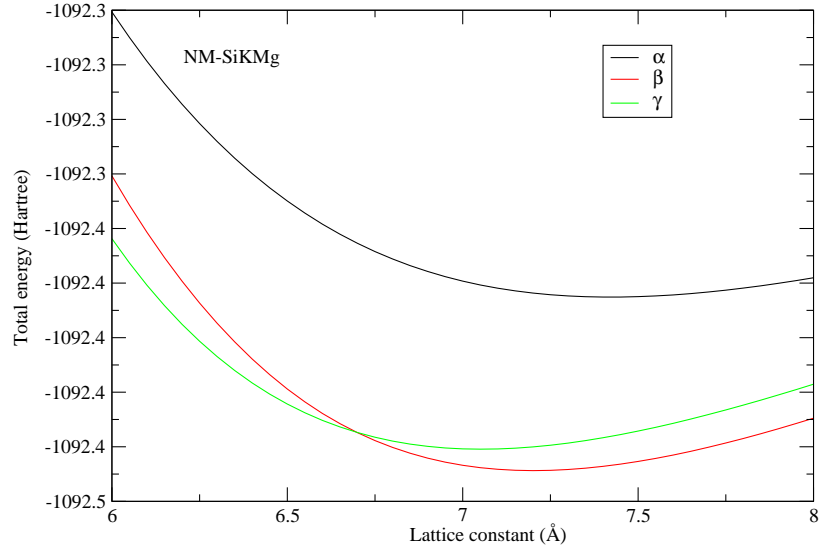
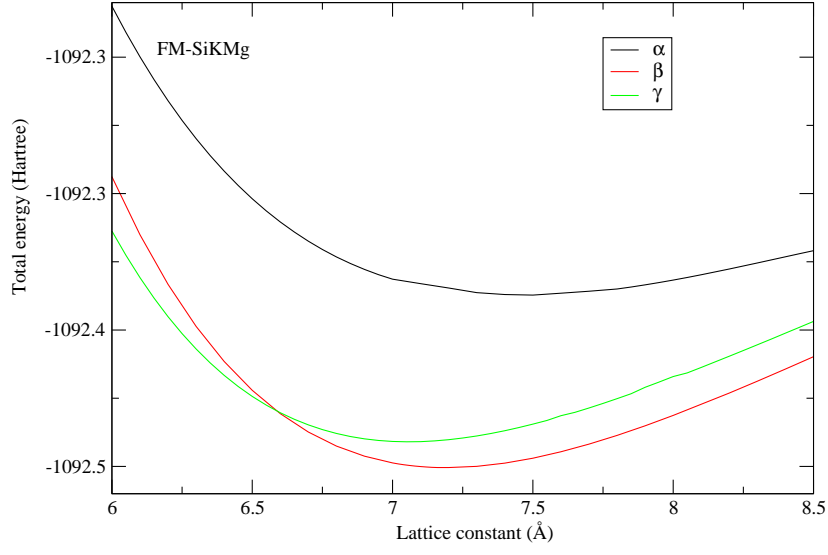


Figure 2: The total energies per unit cell as a function of lattice constants for α , β and γ structure for the SiKMg in the FM phase and NM phase, respectively.

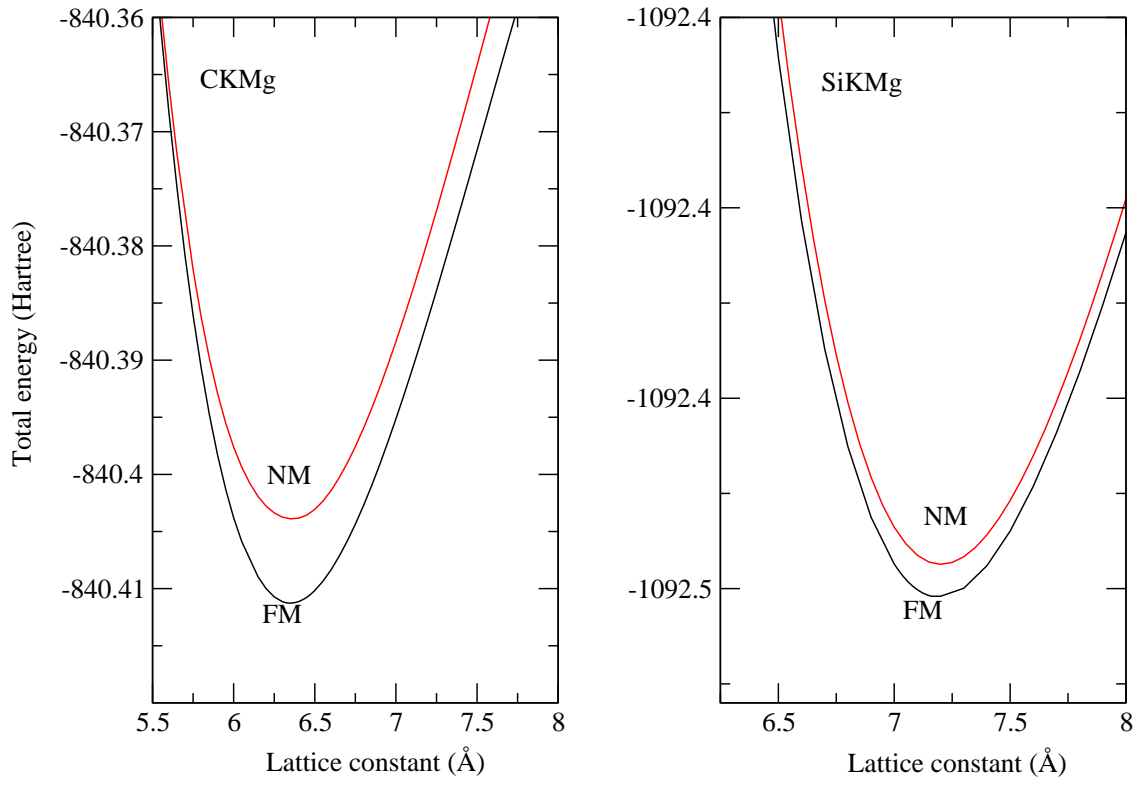


Figure 3: The β -structure total energies of nonmagnetic (NM) and ferromagnetic phase (FM) as a function of the lattice constant for CKMg and SiKMg.

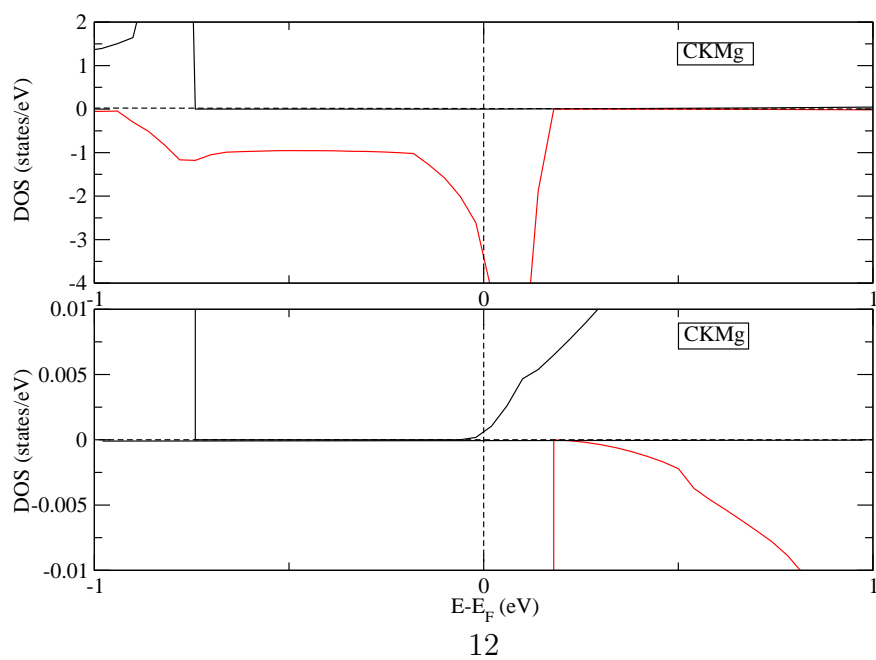
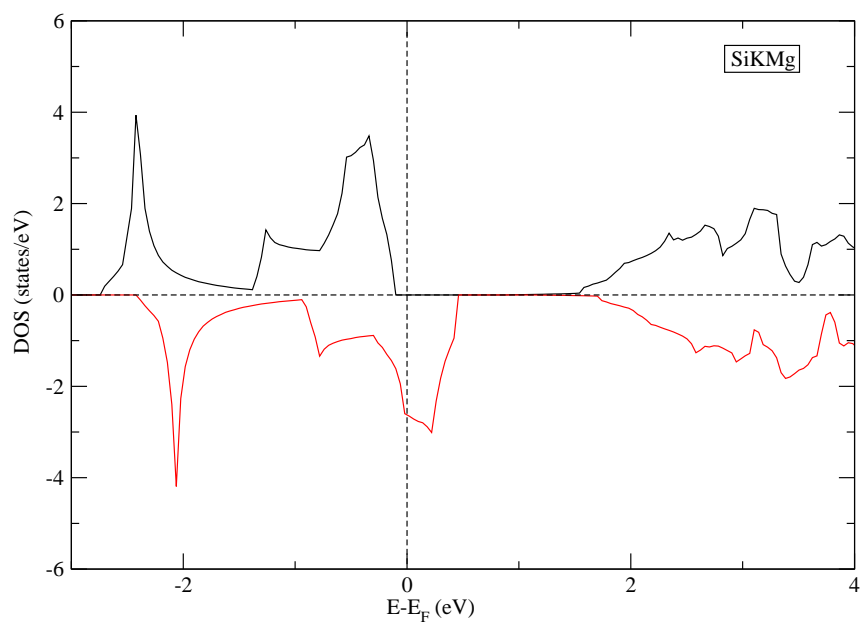


Figure 4: The total DOS for SiKMg and amplified total DOS near the Fermi level for CKMg.

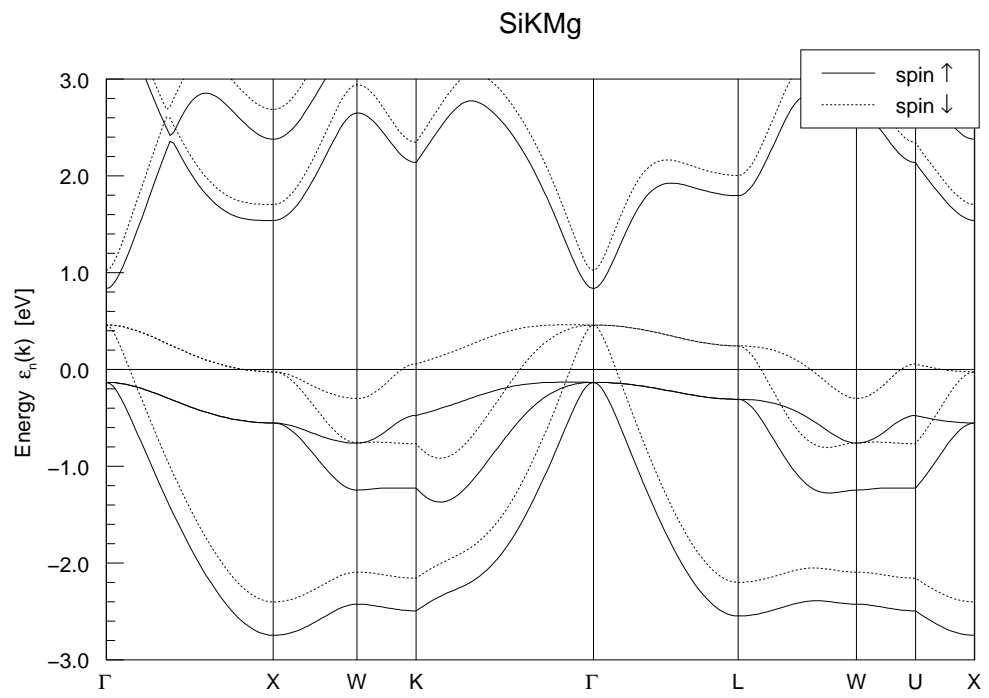


Figure 5: Band structure for SiKMg at equilibrium lattice constant.

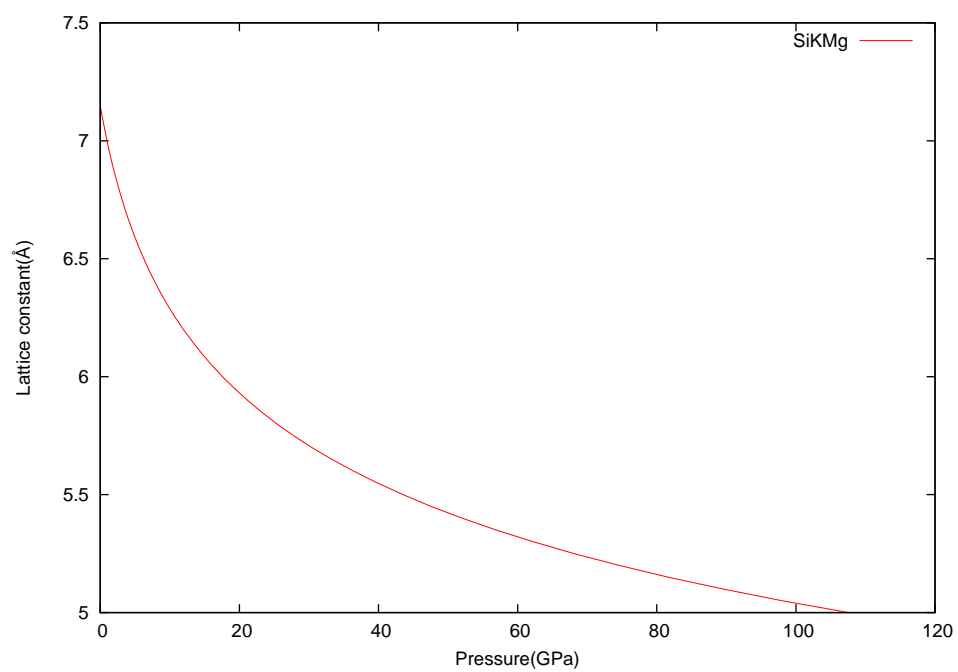


Figure 6: Pressure-lattice constant relation for SiKMg.

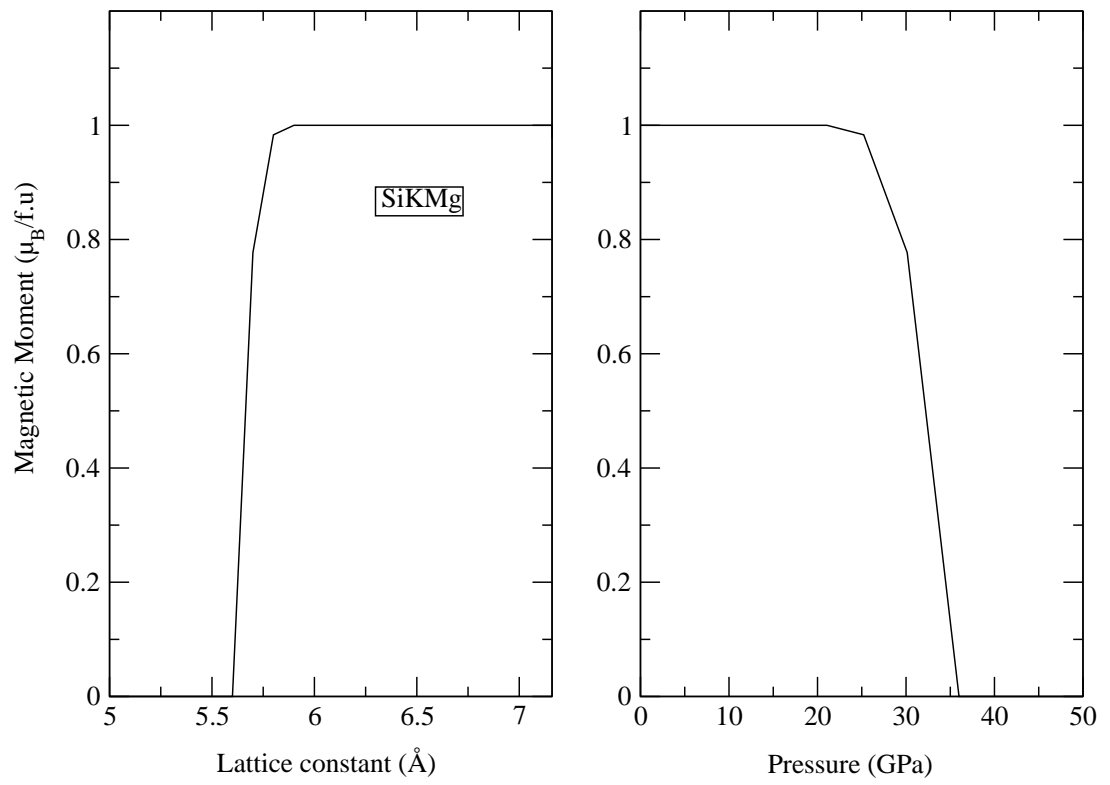


Figure 7: The magnetic moment as a function of the lattice constant and pressure for SiKMg alloy.

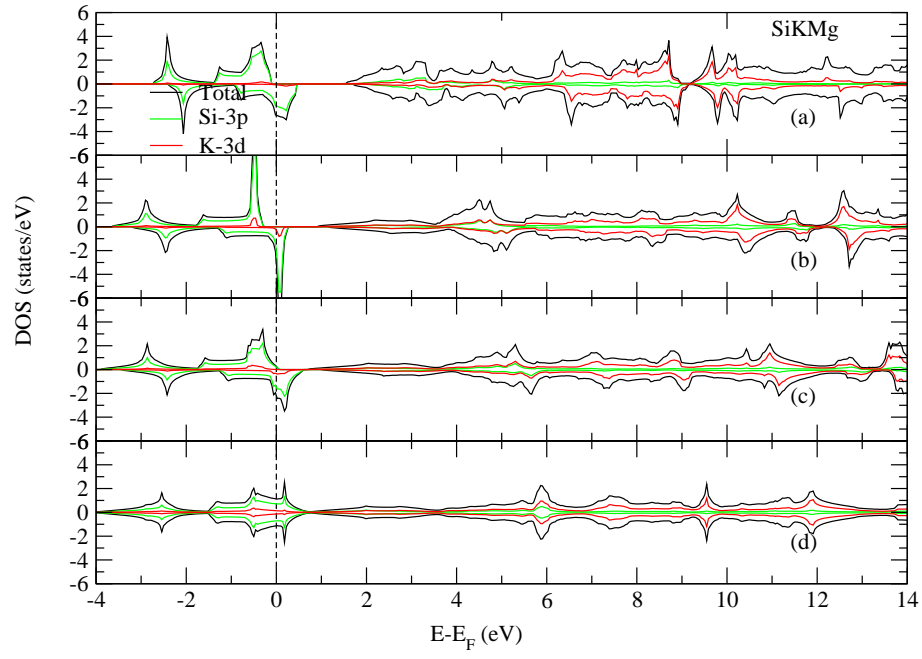


Figure 8: Spin resolved electronic density of states of SiKMg under pressures: (a) 0.00 GPa, (b) 14.56 GPa, (c) 30.14 GPa, (d) 42.95 GPa.

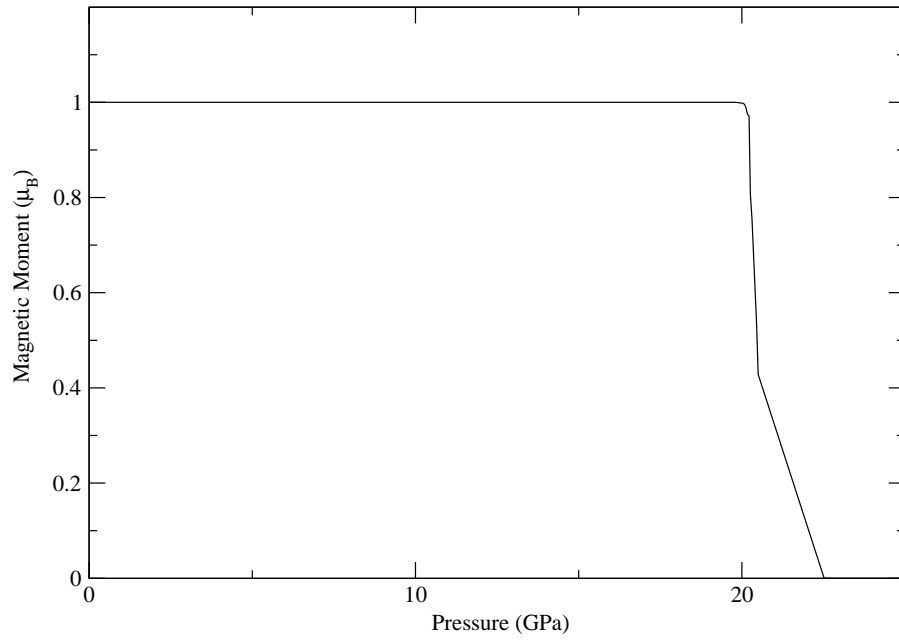


Figure 9: The changes of magnetic moment for CKMg under pressure.

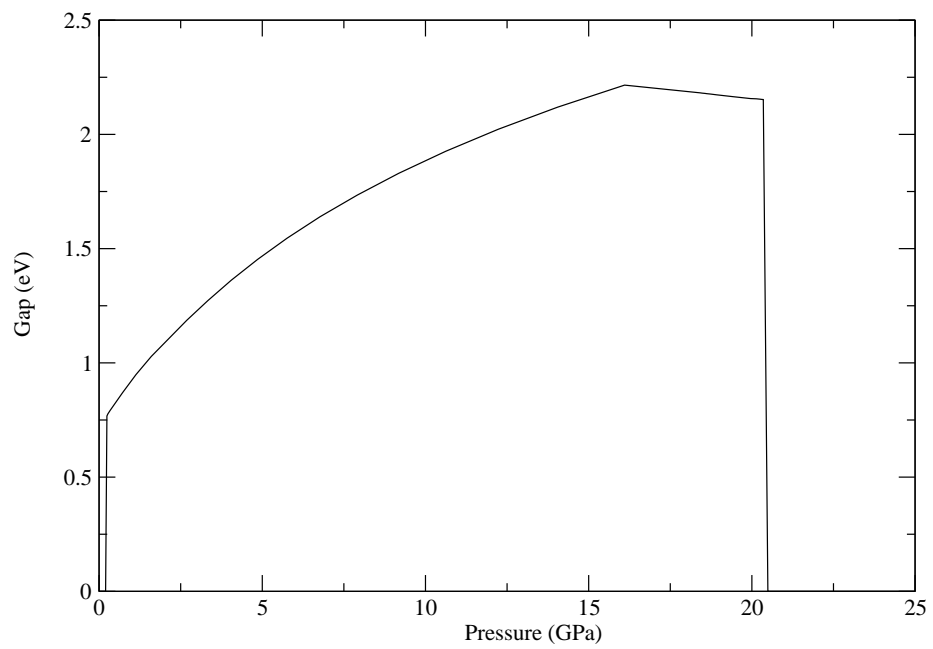


Figure 10: The changes of band gap for CKMg under pressure.